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Silicon nitride materials containing sintering aids and SiO₂, a process for producing them and their use

Background of the Invention

The present invention relates to silicon nitride materials containing sintering aids and 5 SiO₂, a process for producing them and their use.

Ceramic materials are finding ever wider use in the construction of machinery and apparatus, in particular in bearings (Ceramic Airframe Bearings: Lubrications Engineering, 31 (1975), 558-564). All-ceramic bearings have proven useful 10 particularly in applications where there is little lubrication and in corrosive media. However, it has been found in a wide variety of application areas for components made of high-performance ceramic that they degrade and that their life cannot be reliably predicted. The corrosion resistance is dependent to a considerable extent on 15 the type of corrosive medium, the material composition and the superposed mechanical stress. The cause of this is the different reaction behaviour of the individual components of the microstructure of the ceramics (matrix grains, grain boundary phases, impurities) towards acids, bases or under hydrothermal conditions. Liquid-phase-sintered materials such as silicon nitride or silicon carbide (LPSSIC) which contain from 5 to 20% by volume of grain boundary phases display attack 20 along the grain boundary phase in acids and bases. In general, the main point of attack in acid and alkali corrosion in the temperature range <180°C is the grain boundary phase. However, this is not leached out entirely, which is made clear by materials which are corroded through to the centre still having strengths of from 300 to 400 MPa.

The corrosion rates for corrosion in the acid range are strongly dependent on the material composition. EP-A 649 824 discloses that MgO/Al₂O₃-containing materials have good acid resistance without the cause of this behaviour being completely known. One way of further improving the acid resistance of silicon nitride materials containing rare earth metal oxides, Y₂O₃ and possibly Al₂O₃ as sintering aids is to reduce the amount of these sintering aids. However, the resulting improvement in the

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corrosion resistance has to be bought by higher manufacturing costs, since HIP technology is required for densification (EP-A 414 383). Furthermore, Mater. Res. Soc. Symp. Proc. 287 (1993) and Key Engeneering Materials 113 (1996), pp. 227-237, report that corrosion is reduced at very high concentrations of acids, which in
5 the case of phosphoric acid could be explained by formation of a passive layer, see Corrosion of High Performance Ceramics; Springer Verlag, Berlin, 1992; pp. 76 to 78.

There is therefore a great need for acid-stable ceramic materials.
10

It is therefore an object of the invention to provide ceramic materials based on Si_3N_4 which have a high corrosion resistance, i.e., for example, a low mass change and low strength losses after acid treatment.

Description of The Invention

15 It has now been found that a silicon nitride material has, regardless of the way in which it is produced, a high corrosion resistance towards acids if it has a very high SiO_2 content and formation of silicon oxide nitride is avoided, i.e. if the molar ratio of the silicon dioxide in the grain boundary phase to the sintering aids including SiO_2 in the grain boundary phase is >60% and the oxide nitride content ($\text{Si}_2\text{N}_2\text{O}$ content)
20 is <1%.

The invention accordingly provides silicon nitride materials containing sintering aids and SiO_2 and having a molar ratio of the silicon dioxide in the grain boundary phase to the sintering aids including SiO_2 in the grain boundary phase is >60%, preferably
25 >65%, and the oxide nitride content ($\text{SiO}_2\text{N}_2\text{O}$) is <1%.

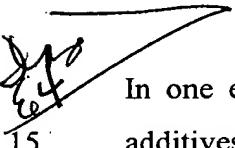
For the purposes of the present invention, sintering aids are the added substances which form the liquid phase during sintering and remain in the grain boundary phase.

30 The grain boundary phase in silicon nitride materials is formed by solidification of the liquid phase present during sintering. It contains the sintering additives, silicon

dioxide and sometimes dissolved silicon nitride. Depending on the conditions of the thermal treatment (cooling rate, etc), it is amorphous or partially crystalline. In general, it wets the silicon nitride particles and forms a three-dimensional network.

5 Sintering aids present in the grain boundary phase for the purposes of the invention are preferably Y_2O_3 , Sc_2O_3 , rare earth metal oxides, alkaline earth metal oxides and Al_2O_3 .

The amount of the added sintering aids + SiO_2 is preferably selected so that the
10 proportion of grain boundary phase in the sintered material is < 20% by volume,
particularly preferably 0.1 - 17% by volume, very particularly preferably from 3 to
15% by volume.


15 In one embodiment of the invention, the silicon nitride materials contain further
additives.

Such additives are, for example, reactive additives, i.e. ones which react with Si_3N_4
and form SiO_2 , for example TiO_2 , WO_3 and/or MoO_3 . Thus, TiO_2 , for example,
reacts to form TiN , while, for example, WO_3 and MoO_3 form silicides with
20 simultaneous oxidation of Si_3N_4 to SiO_2 .

It is likewise possible to use additives which are retained as disperse phases, for
example SiC , TiN , MoSi_2 , TiCN and/or HfO_2 or else additives which form mixed
crystals with the Si_3N_4 , for example AlN .

25 The additives which react with Si_3N_4 and form SiO_2 are preferably present in an
amount of from 0 to 10 mol%, preferably < 5 mol%, based on Si_3N_4 .

30 The additives remaining as a disperse phase are preferably present in an amount of
from 0 to 30% by volume.

Additives which form mixed crystals are preferably present in amounts of from 0 to 50 mol%, preferably <15 mol%, based on Si₃N₄.

In a preferred embodiment of the invention, the porosity of the material is <2%.

5

The invention additionally provides a process for producing the material of the invention, in which, either alone or in combination,

- a) the Si₃N₄ powder used, either alone or together with the sintering aids and, if desired, further additives, is thermally oxidized or
- b) the Si₃N₄ powder, either alone or together with the sintering aids and, if desired, further additives, is tribooxidized during milling or
- c) the Si₃N₄ powder is admixed with sintering aids or with SiO₂ or at least one SiO₂-forming component either before or during milling.

Any commercial Si₃N₄ powder can be used for the processes according to a), b) and c).

20

The thermal oxidation a) is carried out in an oxidizing atmosphere, preferably in air, O₂ and/or water vapour at temperatures of from 300 to 1400°C. In the variant a), a milling step can also be carried out before or after the oxidation.

25

The tribooxidation b) during milling is carried out by intensive milling of the Si₃N₄ powder dry or in a liquid such as H₂O or an organic solvent, e.g. acetone, hexane or alcohol.

30

Milling is preferably carried out in ball mills and is continued until the milled Si₃N₄ has a mean particle size (d₅₀), preferably measured by means of a Master Sizer S, of

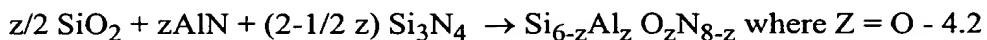
< 2.5 µm, preferably < 1 µm, and has the required molar ratio of SiO₂ to sintering aids.

B
5 In the variant c), the SiO₂-forming components used can be siloxanes, silanes, silicone resins (see Material Science and Technology Vol. 178, Processing of Ceramics, VCH, Weinheim, (1996) Part II, 4-47, DE-A 43 18 974, EP-A 0 412 428, or the reactive additives described, e.g. TiO₂, WO₃ and MoO₃.

10 The amount of SiO₂-forming components is dependent on the desired SiO₂ content of the sintered body.

15 The production of the sintered material from the powder mixtures obtained according to the variants a), b) and/or c) is preferably carried out using generally customary ceramic technology.

20 15 The incorporation of the sintering aids or the additives which form mixed crystals and/or SiO₂ into the silicon nitride crystal lattice can also influence the ratio of SiO₂ to the sintering aids. In this case, when determining the SiO₂/sintering aid ratio, the proportion of the original sintering aids or SiO₂ has to be reduced by the proportion incorporated into the crystal lattice. This is of particular significance in the case of α'- and β'-SiAlONs, e.g. according to the following equation:



25 25 This has to be taken into account when calculating the amounts to be weighed out.

The invention additionally provides for the use of the materials of the invention in the construction of machinery and apparatus, in particular in bearings.

30 30 The following examples serve to illustrate the invention without having any limiting character.
Ex 2
Ex 2

Examples**Example 1**

5 Si_3N_4 powder (Baysinid[®], obtainable from Bayer AG), Y_2O_3 (grade fine, obtainable from H.C. Starck) and Al_2O_3 powder (AKP-50[®], obtainable from Sumitomo) and TiO_2 (P25, obtainable from Degussa) are mixed in amounts corresponding to the composition indicated in Table 1, homogenized in a stirred ball mill in aqueous suspension for 3 hours, spray dried and pressed to form bodies having dimensions of
10 50 x 60 x 8 mm. The particle size (d_{50}) of the mix after homogenization was 0.5 μm , measured by means of a Master Sizer S at pH 11.0. The bodies are baked out at 600°C for 1 hour in air. They are sintered under gas pressure at 1830°C and 50 bar of N_2 for 1.5 hours. The weight losses of the specimens were from <0.3 to 1.8%, depending on the TiO_2 content of the mix. The sintered specimens are cut into test
15 bars and the surfaces were ground.

Mix 1 b was milled for 6 hours at a higher rotational speed in order to increase the oxygen content.

Example 2

This example was carried out using a method analogous to Example 1. The deviations are described below.

25 Examples 2a and 2b were prepared using a method analogous to Example 1b.

The sintering of Example 2a was carried out in a BN-coated graphite crucible in a BN powder bed. The weight loss was 1.8%. In Example 2b, the sample was sintered in an RBSN crucible. The weight loss was 0.2%.

In Example 2c, 1.5% of silicone resin was additionally used as binder. Examples 2e and 2f were produced from silicon nitride powder produced by the plasma method and having a surface area of 60 m²/g and an SiO₂ content of 8%. The specimens were hot pressed at 1800°C.

5

Example 3

The test specimens were produced using a method similar to Example 1. Densification was carried out by a sinter-HIP method, and the weight loss was 10 reduced to < 1.5% by means of the RBSN crucible and a high sample volume/available volume ratio.

Example 4

15 The test specimens were produced using a method analogous to Example 2.

Example 5

20 The test specimens were produced using a method analogous to Example 1, with sintering being carried out at 1800°C.

The respective results are listed in Table 1. By way of example, the mass losses of Examples 1-4 recorded in the corrosion resistance test are shown in Fig. 1.

25 The following measurement methods were employed for determining the data reported in Table 1:

30 Flexural test bars having dimensions of 3 x 4 x 50 mm were cut from the sintered bodies and used to determine the mechanical properties and the corrosion performance.

The strength was determined by means of the 4-point method (support spacing: 20/40 mm).

5 The corrosion performance was determined in thermostated glass vessels using 1 N acid. The acid/solid ratio was >200 ml/10 g of specimen. The acid was changed every 100 hours. The mass loss of the specimens was determined by periodic weighing at defined time intervals (see Δm in Tab. 1). The specimens were rinsed with distilled water and dried before weighing.

10 The oxide nitride content was determined on the specimens by means of XRD measurements. This was carried out using CuK α radiation. The quantitative determination was carried out by means of a Rietveld programme (Refine++). The detection limit was 0.8% by mass of Si₂N₂O.

15 The oxygen content was determined by the hot gas extraction method. The error was <0.1% by mass. The SiO₂ content was calculated from the oxygen content.

20 The porosity was determined in polished sections (prepared as described in Practical Metallography, 27 (1990, 503-513)) at a magnification of 1000 by means of automatic image analysis (Quantiment 570). The proportion by area of the pores in the polished section was taken as the proportion by volume. In parallel thereto, the density was determined by the Archimedes method, in accordance with EN 993-1.

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Table 1 Compositions and corrosion performance of the materials

No.	Additives	SiO ₂ / ^x (additive + SiO ₂) mol%	Si ₂ N ₂ O/(Si ₂ N ₂ O) + βSi ₃ N ₄ Oxide nitride content %	Properties uncorroded		Corrosion conditions	Properties of corroded specimens		
				Porosity	σ4b MPa		Δm(100h), mg/cm ²	Δm(500h), mg/cm ²	σ4b, MPa (500h)
1a	C	5Y ₂ O ₃ 2Al ₂ O ₃ 1 TiO ₂	45	0	<0.5	850	in HCl, 60°C	5.6	8.5
1b	I	5Y ₂ O ₃ 2Al ₂ O ₃ 1 TiO ₂ +SiO ₂	65	0	<0.5	850		0.3	0.3
1c	I	5Y ₂ O ₃ 2Al ₂ O ₃ 5 TiO ₂	74	0	<0.5	825		0.24	0.26
1d	C	5Y ₂ O ₃ 2Al ₂ O ₃ 7.5 TiO ₂	80.4	33	<0.5	800		7.5	9.5
2a	C	5Y ₂ O ₃ 3Al ₂ O ₃	30	0	<0.5	800	in HCl, 60°C	10	16
2b	I	5Y ₂ O ₃ 3Al ₂ O ₃	74	0	<0.5	820		0.2	0.2
2c	I	5Y ₂ O ₃ 3Al ₂ O ₃	72	0	<0.5	800		0.21	0.23
2d	C	5Y ₂ O ₃ 3Al ₂ O ₃	30	0	<0.5	820	in H ₂ SO ₄ , 60°C	9	-
2e	I	5Y ₂ O ₃ 3Al ₂ O ₃ + SiO ₂	63	0	<0.5	725		0.32	0.38
2f	C	5Y ₂ O ₃ 3Al ₂ O ₃ + SiO ₂	81	27	<0.5	765		2.2	8.3
3	I	5Y ₂ O ₃ 1.5 Al ₂ O ₃ + 0.5 TiO ₂	63	0	<0.5	800	in H ₂ SO ₄ , 60°C	0.35	0.5
4	C	3Y ₂ O ₃ 1.8 Al ₂ O ₃	75.3	12	<0.5	730		1.4	4.5
5a	I	3MgO 2 Al ₂ O ₃	75	0	<0.5	820	in H ₂ SO ₄ , 60°C	0.1	0.1
5b	C	3MgO 2 Al ₂ O ₃	45	0	<0.5	730		0.3	0.45

C = comparative example; I = example according to the invention
 2a mass loss on sintering = 1.6%; 2b mass loss on sintering = 0.2%
 x in the grain boundary phase

Discussion of the results:

The material described in EP-A 649 824 was reproduced in Example 1 without controlling the oxygen content and, under our conditions, displays a mass loss of 8.5 mg/cm². Setting the SiO₂ content leads to an improvement in the corrosion performance of nominally identical materials by a factor of 30 (as demonstrated by Examples 1a and 1b). The importance of controlling the oxygen content not only in preparation of the mix is shown by comparison of Example 2a with Examples 2b and 2c. While sintering of the material in Example 2a leads to a high weight loss which drastically reduces the SiO₂ content of the sintered material, specimens which were sintered under controlled conditions and have a small weight loss (2b and 2c) display the favourable corrosion performance sought.

It is found that the high SiO₂ content leads to a change in the corrosion kinetics. While conventional materials have a linear relationship between corrosion layer thickness and reaction time up to corrosion layer thicknesses of several 100 µm, in the case of the materials of the invention, passivation occurs after only a few µm reaction depth (Fig. 2). This passivation occurs all the more quickly, the lower the additive content and the lower the grain size of the silicon nitride grains in the material.